

vergence of $P'(x,t)$ since each term of the series representing $P_2(x,t)$ is in absolute value equal to or less than the corresponding terms of the series representing $P'(x,t)$.

It is a simple matter now to show that the series representations of $\partial P'_2/\partial t$, $\partial P'/\partial t$ and $\partial^2 P'/\partial x^2$ are all uniformly convergent. The series representation of $\partial P_2/\partial t$ is equal to the sum of the two uniformly convergent series representing HP and $-HP_2$. The terms of the series representing $\partial P'/\partial t$ are in absolute value less than the terms of the uniformly convergent series representing $\partial P_2/\partial t$, hence the series representing $\partial P'/\partial t$ is uniformly convergent by the M-test. Finally, the series representing $\partial^2 P'/\partial x^2$ is equal to the sum of the two

uniformly convergent series representing $(1/\alpha) \cdot (\partial P'/\partial t)$ and $(1/\alpha)(V_2/V_1)(\partial P_2/\partial t)$. We have shown then that the term-by-term differentiation of the series representing P' and P'_2 , both with respect to x and t (twice with respect to x) is justified; furthermore, we have shown that the solutions $P'(x,t)$ and $P_2(x,t)$ satisfy the partial differential equations—equations 1B and 2B.

That the solutions satisfy the boundary conditions—equations 3B and 4B—may be verified by inspection. The authors have verified that the solutions also satisfy the initial conditions—equations 5B and 6B—by substitution; consequently, the validity of the series of residues is established. Furthermore, the solution is unique.

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VISCOSITY-CONCENTRATION AND FLUIDITY-CONCENTRATION RELATIONSHIPS FOR SUSPENSIONS OF SPHERICAL PARTICLES IN NEWTONIAN LIQUIDS

By T. F. FORD¹

It was established by Bingham² that plots of fluidity against concentration tend to be linear over considerable concentration ranges, whereas viscosity plots are always curved. Many illustrations, for proteins, have been given by Treffers.³ DeBruijn⁴ and Vand^{5b} have made use of such plots. In general, however, the fluidity function has received little attention, despite the first order reciprocal relationship between the linear equation $\phi/\phi_0 = 1 - 2.5C_v$ (I) and the Einstein equation as usually written $\eta/\eta_0 = 1 + 2.5C_v$ (II). It is the purpose of this paper to show that the consensus of present theoretical and empirical equations for the flow of suspensions of rigid spherical particles alone makes I a closer approximation than II, and by re-examination of available data to support this conclusion to the extent it may even be suggested that equation I and its exact reciprocal, $\eta/\eta_0 = 1 + 2.5C_v + 6.25C_v^2 + \dots$ (III) may describe accurately the flow of suspensions of rigid spheres in Newtonian liquids at low and moderate concentrations.

Collected Viscosity Equations and Their Reciprocal or Fluidity Forms

Various equations relating viscosity to concentration for suspensions of spheres are listed in Table I, together with the reciprocal or fluidity forms of each. For ready comparison all equations are given in Table I as power series, $Y = 1 + aC_v + bC_v^2 + cC_v^3$

+ ...,⁶ where Y designates either relative viscosity, η/η_0 , or relative fluidity, ϕ/ϕ_0 , and C_v is the volume fraction of the dispersed phase. The several pairs of equations are exactly equivalent and are obtained, the one from the other, by long division. The over-all purpose of the table is to show that without regard to theoretical or experimental background all of these equations are more nearly linear in the fluidity form.

It is seldom noted that Einstein's derivation⁷ really led to the equation $\eta/\eta_0 = (1 + 0.5C_v)/(1 - C_v)^2$, from which the series given in Table I are derived. This equation takes no account of interactions between particles. It applies, therefore, over concentration ranges in which interactions can be disregarded; but these ranges may be considerably wider than those to which the simplified form, II, applies.

Interactions between particles have been considered by various authors, in particular Simha and co-workers (cf. ref. 8), DeBruijn,⁴ and Vand.^{5a} DeBruijn,⁴ with Burgers,⁹ give a derivation which is unique in utilizing the fluidity function and is semi-independent of Einstein's. DeBruijn obtains $\phi/\phi_0 = 1 - 2.5C_v + 2.5kC_v^2$. He evaluates the constant k in an empirical way by making $\phi/\phi_0 = 0$ at $C_v = 0.74$, the volume fraction occupied by

(1) Naval Research Laboratory, Washington, D. C.

(2) E. C. Bingham, "Fluidity and Plasticity," McGraw-Hill Book Co., Inc., New York, N. Y., 1922.

(3) H. P. Treffers, *J. Am. Chem. Soc.*, **62**, 1405 (1940).

(4) H. DeBruijn, *Rec. trav. chim.*, **61**, 863 (1942); Proceedings of the International Congress of Rheology, Amsterdam, 1949, p. II-95.

(5) V. Vand, (a) *THIS JOURNAL*, **52**, 277 (1948); (b) **52**, 300 (1948).

(6) A catalog of viscosity equations converted to power series is also given by Bredée and de Booy. Their list includes several earlier forms omitted here. H. L. Bredée and J. deBooy, *Kolloid Z.*, **79**, 31 (1937).

(7) A. Einstein, (a) *Ann. Physik*, **19**, 286 (1906); (b) **34**, 591 (1911).

(8) R. Simha, (a) *THIS JOURNAL*, **44**, 25 (1940); (b) *J. Applied Physics*, **23**, 1020 (1952).

(9) J. M. Burgers, "First and Second Report on Viscosity and Plasticity," N. V. Noord-Hollandsche Uetgeversmaatschappij, Amsterdam, Holland, 1938.

TABLE I
EXPRESSIONS RELATING RELATIVE VISCOSITY AND RELATIVE FLUIDITY TO VOLUME CONCENTRATION FOR SUSPENSIONS OF RIGID SPHERICAL PARTICLES

Author	Year	Ref.	Theoretical equations	
			Viscosity form	Fluidity form
Einstein	1906-11	(7)	$\eta/\eta_0 = 1 + 2.5C_v + 4C_v^2 + 5.5C_v^3 \dots$	$\phi/\phi_0 = 1 - 2.5C_v + 2.25C_v^2 - 1.25C_v^3 \dots$
DeBruijn	1942	(4)	$1 + 2.5C_v + 4.7C_v^2 + 7.77C_v^3 \dots$	$1 - 2.5C_v + 1.552C_v^2 \dots$
Simha	1948	(5a)	$1 + 2.5C_v + 7.349C_v^2 \dots$	$1 - 2.5C_v - 1.099C_v^2 \dots$
Simha ^a	1952	(8b)	$1 + 2.5C_v + 3.73C_v^2 + 6.94C_v^{7/2} \dots$	$1 - 2.5C_v + 2.52C_v^2 - 6.94C_v^{7/2} \dots$
Kynch ^a	1956	(10)	$1 + 2.5C_v + (7.5 \text{ to } 6.75)C_v^2 \dots$	$1 - 2.5C_v - (1.25 \text{ to } 0.50)C_v^2 \dots$
Empirical equations				
Arrhenius	1887	(11)	$1 + 2.5C_v + 3.125C_v^2 + 2.60C_v^3 \dots$	$1 - 2.5C_v + 3.125C_v^2 - 2.60C_v^3 \dots$
Simha	1948	(5b)	$1 + 2.5C_v + 7.17C_v^2 + 16.2C_v^3 \dots$	$1 - 2.5C_v - 0.92C_v^2 + 4.0C_v^3 \dots$
Robinson	1949	(16)	$1 + 2.5C_v + 4.6C_v^2 + 8.4C_v^3$	$1 - 2.5C_v + 1.65C_v^2 - 1.0C_v^3 \dots$

^a Both Simha's and Kynch's second and higher order coefficients change with concentration. The equations given are for dilute solutions. See text.

close-packed uniform spheres. This makes $k = 6209$ and gives the equations attributed to DeBruijn in the table. It will be seen in the discussion of experimental results, however, that for rigid particles it is more probable that $\phi/\phi_0 = 0$ at $C_v = 5236$, the volume fraction in cubical packing. Imposing this condition makes $k = 0.222$ and the two equations become $\eta/\eta_0 = 1 + 2.5C_v + 5.123C_v^2 + 9.99C_v^3$ and $\phi/\phi_0 = 1 - 2.5C_v + 1.127C_v^2$, respectively.

DeBruijn's and Vand's equations both represent attempts to fit the complete concentration range. Recently Simha^{5b} and more recently Kynch¹⁰ have deduced that the constants of the higher power terms must change with concentration. The equations attributed to Simha in the table are expansions of one of his theoretical equations (7a) applicable at low concentrations, up to $C_v = 0.065$. His equation contains a parameter defined by the relationship $f^3 = 8C_{\text{max}}$, where C_{max} may be either that corresponding to cubical packing, $C_v = 0.5236$ ($f = 1.61$), or to close packing, $C_v = 0.74$ ($f = 1.81$). In evaluating the constants for Table I cubical packing has been assumed. In his discussion Simha notes that to fit experimental data over the whole concentration range, f must actually change from a value around 1.3 to less than 2. His final evaluation thus becomes semi-empirical.

Kynch's derivative differs from Simha's but the final result is about the same. Kynch states that a popular value for the second order constant in the viscosity equation is 6.25. This makes the second order constant zero in the fluidity form. According to Simha's treatment the second order constant 2.5 is possible, requiring only that f be given the value $\sqrt[3]{2.5}$ or 1.357. Kynch's observation is of interest in the light of statistical analyses to be presented in the next section of this paper.

The empirical equation due to Arrhenius¹¹ is usually written in $\eta/\eta_0 = kC_v$. For inclusion in the table it has been rewritten as $\eta/\eta_0 = e^{kC_v}$, expanded in the series $\eta/\eta_0 = 1 + kC_v + k^2C_v^2/2! + k^3C_v^3/3! + \dots$, and the constant k arbitrarily assigned the value 2.5.

The second and third order constants in the empirical equation assigned to Robinson in Table I are averages based on three extrapolated experi-

mental values of sediment volumes for glass spheres, 1.77, 1.81 and 1.88, given by him. The reciprocals of these numbers, 0.565, 0.553 and 0.532, compare well with the volume fraction of uniform spheres in cubical packing, $(4/3\pi^2)/(8\pi^2)$ or 0.5236.

Review of Experimental Results

Viscosity measurements which are sufficiently extensive and rigorous for mathematical analysis and on systems acceptable as models of suspensions of spherical particles are scanty. No data yet reported are adequate in all respects. This arises in part from uncertainties as to concentration and shape in molecular and colloidal solutions, and in part from uncertainties in correcting results on visible particles for effects due to size alone. The experiments here considered were selected for various reasons, some merely because prominence previously given them demands their inclusion. In every case the original data were carefully scrutinized and recalculated. Insofar as justified, statistical methods were applied since the purpose was refinement of precision in establishing the constants in the type equation $Y = 1 + aC_v + bC_v^2 + cC_v^3 + \dots$.

Bancelin's Experiments on Gamboge Sols.—Bancelin's experiments¹² are the first in point of time and apparently were performed very carefully. He prepared monodisperse suspensions of gamboge by centrifugation (the method of Jean Perrin), and for each fraction determined viscosities at various concentrations. Bancelin's object was to test the Einstein equation which as then published was $\eta/\eta_0 = 1 + C_v$. He obtained as his average result $\eta/\eta_0 = 1 + 2.9C_v$. He therefore wrote to Einstein who informed him that the equation should have been $\eta/\eta_0 = 1 + 2.5C_v$. Bancelin's paper gives values for a suspension containing particles 0.30μ in diameter, at six concentrations between 0.0024 and 0.0211 ml. per ml. Least squares analysis of these data, using the type equation $Y = k + aC_v$, gives

$$\eta/\eta_0 = 0.9994 + 2.715C_v \quad (\text{S.E.E., } 0.00069)$$

and

$$\phi/\phi_0 = 1.0000 - 2.549C_v \quad (\text{S.E.E., } 0.00052)$$

Here, the numbers in parentheses are the standard errors of estimate of Y , a convenient measure of the

(10) G. J. Kynch, *Proc. Roy. Soc. (London)*, **A237**, 90 (1956).

(11) S. Arrhenius, *Z. physik. Chem.*, **1**, 285 (1887).

(12) M. Bancelin, *Compt. rend.*, **152**, 1382 (1911).

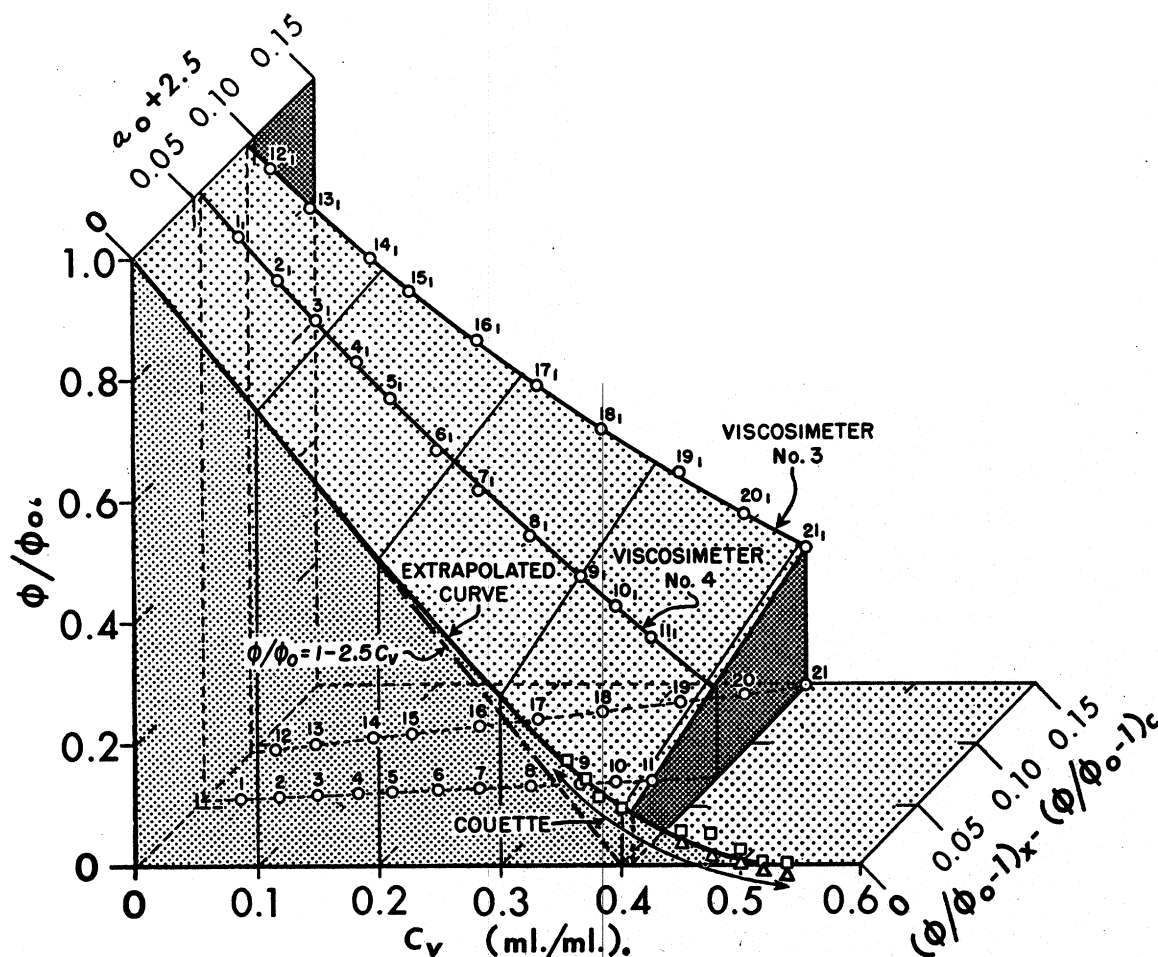


Fig. 1.—Fluidity-concentration plots for suspensions of 125–205 μ diameter glass beads, data by Vand.^{5b} Points for stirred suspensions (Couette) indicated by open triangles, for non-stirred suspensions by open squares. The method of extrapolation is described in the text.

fit.¹³ These results show that to a close approximation, for these data $k = 1$, a necessary check, and that the experimental first order constant is much closer to 2.5 than to 2.9 as reported by Bancelin and repeatedly quoted since.

The data cover a low concentration range. Nevertheless, the measures of deviation given above indicate that over this concentration range the fluidity function is the more linear.

It is possible that for Bancelin's gamboge the experimental first order constant was actually about 2.55, considering that errors in effective volume concentration, due to slight departure from the spherical shape, for example, would be positive. If the concentrations be corrected accordingly by the factor 2.55/2.5, the data are now fit by

$$\eta/\eta_0 = 1 + 2.5C_v + 6.75C_v^2 \quad (\text{S.E.E., } 0.00053)$$

and

$$\phi/\phi_0 = 1 - 2.5C_v - 0.1C_v^2 \quad (\text{S.E.E., } 0.00052)$$

Experiments on Suspensions of Glass Spheres.—Suspensions of glass spheres have been used as model systems by Eirich, Bunzl and Margaretha,¹⁴ Eirich

and Goldschmidt,¹⁵ Vand,^{5b} Robinson,¹⁶ and Eveson and Whitmore (ref. 10).

The experiments by Eirich, *et al.*, which were on yeast cells and mushroom spores as well as glass beads, are generally credited with establishing the first order constant within limits of ± 0.3 by use of capillary viscosimeters, and within limits of ± 0.2 by use of the Couette viscosimeter. The glass spheres used by Eirich, *et al.*, were from 0.0125 to 0.0205 cm. in diameter. Subsequent to their experiments it has been pointed out by Vand (*vide infra*) that use of particles of this size requires appreciable corrections of both C_v and $\phi/\phi_0 - 1$, by factors which are related to the dimensions of the viscosimeters. Such corrections cannot be applied with assurance to Eirich's capillary data, but they can be applied to the Couette data, and the Couette data are for a low concentration range, $C_v = 0.01$ to 0.08, not adequately covered by other workers with glass beads. A large scale plot of these data discloses that they do not extrapolate to $\phi/\phi_0 = 1$ at $C = 0$; and least squares analysis indicates that the C_v values are too low by the constant amount $\Delta C_v =$

(13) The standard error of estimate is the square root of the mean of the squared deviations, $S_y = \sqrt{\sum d^2/N}$. Other measures of the fit, mean deviations, standard deviations, and coefficients of correlation, agreed with the standard errors of estimate.

(14) F. Eirich, M. Bunzl and H. Margaretha, *Kolloid. Z.*, **74**, 276 (1936).

(15) F. Eirich and O. Goldschmidt, *ibid.*, **81**, 7 (1937).

(16) J. V. Robinson, (a) *THIS JOURNAL*, **53**, 1042 (1949); (b) **55**, 455 (1951).

10, approximately. The C_v values adjusted by amount and the observed $\phi/\phi_0 - 1$ values were corrected by the use of formulas later developed by J. S. Thus corrected the data are fit by the equation $\phi/\phi_0 = 1 - 2.50C_v + 0.95C_v^2$, S.E.E., 15. The data as given are fit by the equation $\phi/\phi_0 = 1 - 2.39C_v + 3.29C_v^2$, S.E.E., 0.0018. These experiments by Eirich, *et al.*, provide a second close check of the first order constant, 2.5.

Vand^{5b} used the same glass beads as Eirich, *et al.*, loaned to him by Prof. Eirich, but he suspended them in a more viscous liquid, made other refinements in technique, and extended the concentration range almost to saturation. Vand gives an average diameter of 0.013 cm. for these beads. Like Eirich, *et al.*, he used two Ostwald viscosimeters, of different bore diameters, and a Couette viscosimeter, the Couette machine only at concentrations of 35% and higher.

Vand multiplied all of this C_v and $\phi/\phi_0 - 1$ values by specific correction factors for each instrument, and finally combined his corrected data as a composite plot. His final equation is designed to fit a smooth curve through these points. Inclusion of the Couette results has been criticized by Kynch¹⁰ on theoretical grounds. The data themselves, however, provide sufficient reason for their reexamination. With both the Couette and Ostwald instruments, at concentrations beginning immediately above $C_v = 0.35$, different viscosities were obtained depending on whether the suspensions were stirred or not. These known deviations are greater than the total deviations at lower concentrations. This fact is itself sufficient to exclude most of the Couette data, and some of the Ostwald data, or at least to diminish the weight to be given these data. It is noted also that Vand's corrected values for his two Ostwald viscosimeters fall more nearly on smooth curves if plotted separately than if combined. This was confirmed by comparison of the fit of second order equations obtained by least squares analysis. The deviation of the two curves indicates a more empirical analysis than used by Vand.

A method of blind extrapolation in the direction of zero corrections is illustrated by Fig. 1. Here smooth curves through the original uncorrected Ostwald points are drawn in the two receding vertical planes, and the corrected Couette values and the extrapolated Ostwald curve are shown in the plane of the paper. The positions of the receding vertical planes are determined as follows: at $C_v = 0$ by requiring that the first order constants, 2.445 and 2.405, found in the usual way by plotting $(\phi/\phi_0 - 1)/C_v$ against C_v , shall extrapolate to 2.5 for an infinite capillary; and at $C_v = 0.35$ by placing the experimental Ostwald $\phi/\phi_0 - 1$ values, 0.760 and 0.680, and the corrected Couette value, 0.820, on a straight line. The two Ostwald curves thus placed in space and extrapolated into the plane of the paper give a third curve for which the corrections are certainly reduced.

The assumptions involved are: (1) That the first order constant is in fact 2.5. This is supported experimentally by Bancelin's and Eirich's results. (2) That the Couette fluidity used at $C_v = 0.35$ is

approximately correct. This seems justified within limits by the apparent absence of stirring errors at this concentration, and by the fact the Couette corrections are in any case small (roughly one-fifth to one-tenth of the Ostwald corrections). (3) That the effective or total corrections vary not only with bore diameter, but also with concentration. This is supported by the observations that Vand's $\phi/\phi_0 = 1$ corrections, for wall effects, are in fact averages of values which apparently vary, approximately linearly, by as much as 12% over the range $C_v = 0.05$ to 0.35.

The extrapolations actually were performed analytically. Interpolated fluidities for the two Ostwald viscosimeters at concentrations increasing by 5% were taken from large scale plots, and also calculated from the second order equations fit to the original data by least squares. Using the analytically interpolated Ostwald values and referring the extrapolation at $C_v = 0.35$ to the corrected Couette values (Fig. 1), the extrapolated curve is fit over the range $C_v = 0.05$ to 0.35 by the equation

$$\phi/\phi_0 = 1 - 2.5C_v - 0.11C_v^2 + 1.6C_v^3$$

Referring the extrapolations to the uncorrected Couette values the equation is

$$\phi/\phi_0 = 1 - 2.5C_v - 0.08C_v^2 + 1.9C_v^3$$

The graphically interpolated values give essentially the same constants. The uncertainty in the second order constant is ± 0.10 , approximately. Although the type equation $Y = 1 \pm 2.5C_v + bC_v^2 + cC_v^3$ is used here, the extrapolated curves are fit equally well, over most or all of the range $C_v = 0.05$ to 0.35, by equations of the form $\phi/\phi_0 = 1 - 2.5C_v + dC_v^4$.

While the above described extrapolations, based on the uncorrected data, seem to avoid many assumptions, they also include a certain error. This is because in the polynomial equations used the concentration and all multipliers of it are involved as powers higher than the first. It is noted, however, that the C_v corrections (multipliers) as calculated by Vand are less than half his $\phi/\phi_0 - 1$ corrections for wall effects; and it is noted also that it is only in the latter and not in the concentration corrections that any reason for variation with concentration is apparent. Accordingly, Vand's corrected C_v values were combined with his uncorrected $\theta/\theta_0 - 1$ values, and the various manipulations repeated. Referring the extrapolations to the corrected C_v and corrected $\theta/\theta_0 - 1$ Couette values at $C_v = 0.35$, for the range $C_v = 0.05$ to 0.35 the equation obtained is

$$\phi/\phi_0 = 1 - 2.5C_v + 0.00C_v^2 + 1.4C_v^3$$

Referring the extrapolations to the corrected C_v and uncorrected $\phi/\phi_0 - 1$ Couette values the equation is

$$\phi/\phi_0 = 1 - 2.5C_v + 0.11C_v^2 + 1.5C_v^3$$

The uncertainty in the second order constant is 0.10, approximately.

The foregoing calculations all indicate that within the apparent accuracy of the data, in an equation of the form $\phi/\phi_0 = 1 - 2.5C_v + bC_v^2 + cC_v^3 + \dots$, the second order constant "b" is numerically small, and may be zero.

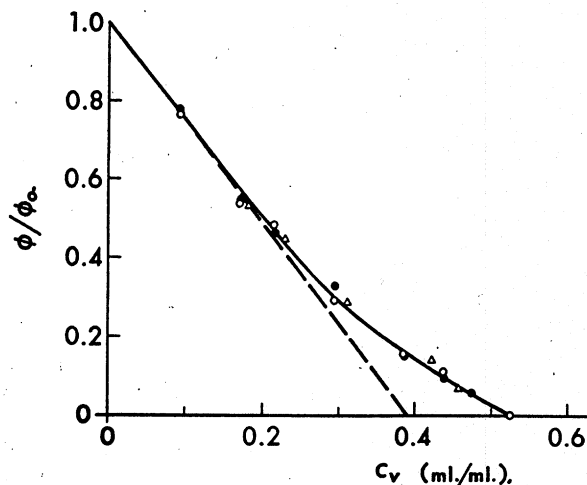


Fig. 2.—Fluidity-concentration plot for suspensions of glass beads, 10–30 μ diameter, in no. 30 motor oil (open circles), no. 50 motor oil (closed circles), and castor oil (open triangles). Data are by Robinson.^{17a}

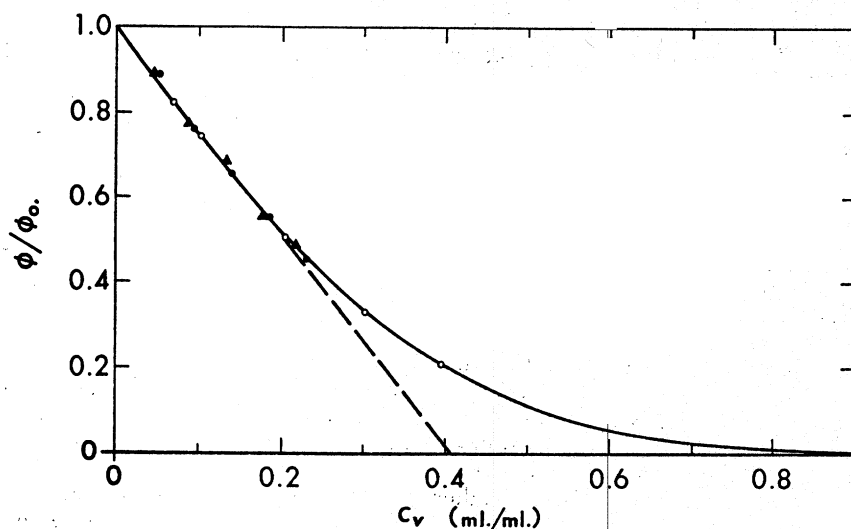


Fig. 3.—Fluidity-concentration plot for milk fat suspensions in fat-free milk serum. Three sets of data are by Leviton and Leighton.²⁰ The solid curve drawn through the points is that determined by the theoretical equation developed by these authors. Compare the experimental points with those for rubber latex, Fig. 4.

Robinson used beads 3 to 30 μ in diameter, an order of magnitude smaller than Eirich's and Vand's beads, suspended both in oils^{16a} and in water-glucose solutions.^{16b} He used a Couette viscosimeter. The fluidity plot for his oil suspensions is shown in Fig. 2. Corrections according to Vand's formulas have been applied, but practically the identical curve is given by the uncorrected data. Both this plot and the similar plot for the water-glucose suspensions confirm the general shape of the Vand extrapolated and Couette curve of Fig. 1, and particularly the final intercept in the neighborhood of $C_v = 0.5236$. It will be recalled that Robinson's sediment volumes, obtained by centrifugal packing, also indicate approximately this value.

Sven Odén's Experiments on Sulfur Sols.—Sven Odén's viscosity measurements on sulfur sols¹⁷ do not support statistical analysis. The first

order constants obtained graphically vary from 2.95 to 4.29, depending on particle size and temperature. Odén used two size fractions, containing particles about 10 μ and 100 μ in diameter, and temperatures from 5 to 40°. It is found that plots of the first order constants against temperature extrapolate to 2.5 at 95°, approximately, for both sizes of particles. Except in this indirect way Odén's results contribute little as a check of the Einstein equation.

The temperature extrapolations are of interest in connection with shells of bound water, postulated by Hatschek¹⁸ to explain the deviations noted. The implication above is that the shells disappear at 95°. It seems plausible, however, that shape factors are involved, the particles becoming more spherical as they approach the melting point.

Milk Fat, Latex, and Asphalt Emulsions.—Data on suspensions of milk fat (cream) variously diluted with fat-free milk serum, by Leviton and Leighton,¹⁹ are plotted in Fig. 3. One of their four sets of data has been omitted because the viscosity

of the serum was made much higher than for the other three by addition of cane sugar. The curve drawn through the points (Fig. 3) is that determined by a theoretical equation²⁰ derived by the authors. This equation takes account of the fact that milk fat is liquid,²¹ by making use of Taylor's correction of Einstein's constant 2.5 for sympathetic flow inside liquid particles. This correction lowers the theoretical first order constants to 2.44, 2.45 and 2.39, respectively, for the three sets of data; the average experimental value is 2.44, corresponding to a linear intercept at $C_v = 0.41$ as drawn. Although the dimensions of the viscosimeters are not given, and therefore correction by Vand's formulas is not attempted, the particles are so small these corrections would be negligible in any case. This is confirmed by Leviton and Leighton's comparison of two emulsions containing particles 3 μ and 0.7 μ in diameter, for which exactly the same viscosities were obtained.

These data again confirm the Einstein first order constant, as well as Taylor's correction, but they indicate a final intercept well beyond $C_v = 0.5236$. Since milk fat particles are liquid as well as spherical they should be sufficiently deformable to roll, one over the other, and therefore flow past the concentration corresponding to cubical packing is to be

(18) E. Hatschek, *Kolloid Z.*, 7, 301 (1910); 11, 280 (1912).

(19) A. Leviton and A. Leighton, *THIS JOURNAL*, 40, 71 (1936).

(20) Expanded as a polynomial this equation is $\phi/\phi_0 = 1 - 2.44W + 2.98W^2 - 2.4W^3 + \dots$ where $W = C_v + C_v^2/2 + C_v^3/6$.

(21) Viscosity 14 centipoises.

(17) S. Odén, *Z. physik. Chem.*, 80, 709 (1912); "Der Kolloide Schwefel," *Nova Acta Regiae Soc. Sci. Upsaliensis*, (4) 3 (1913).

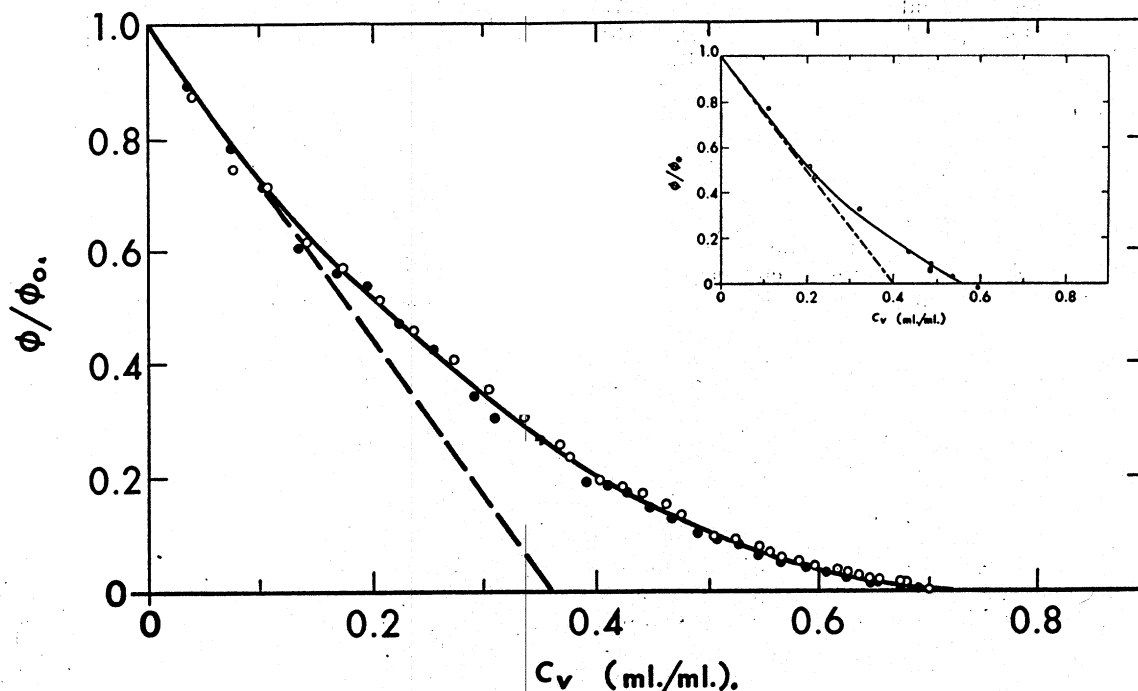


Fig. 4.—Fluidity-concentration plots for rubber latex (main plot) and asphalt emulsions (inserted box). Latex data are by Rhodes and Smith²²; asphalt data by Eilers.²³ Independent sets of data are indicated by different types of points.

expected. Cream can be concentrated to 72 to 74% by centrifuging at room temperature, and an actual intercept in this neighborhood seems possible.

Fluidity plots for two natural rubber latexes and for two asphalt emulsions, derived from data by Rhodes and Smith,²² and Eilers,²³ respectively, are shown in Fig. 4. Both of these sets of data have been used in connection with derivations of viscosity equations. In Fig. 4 the latex data are plotted as given by the authors, since a Hoespler viscosimeter was used and Vand's corrections therefore do not apply. The first order constant calculated for the latex curve is about 2.8, and the final intercept is in the neighborhood $C_v = 0.74$. Both results are reasonable. Latex particles are often not spherical, may be pear shaped, and may even have tails: therefore, the first order constant could well include a shape factor. Latex particles also are plastic and deformable. These experiments are, therefore, of little value as a check of the Einstein equation.

The asphalt data, inserted box of Fig. 4, were first corrected by use of Vand's formulas. The corrections are necessarily approximate. Eilers' particle sizes range from less than 1.6μ to 9.7μ in diameter: a diameter of 5.6μ based on the average particle volume was used. Eilers gives three capillary diameters and apparently reports average viscosities obtained with the three instruments: therefore, average C_v and $\phi/\phi_0 - 1$ corrections were applied. Thus corrected a first order constant of 2.3, approximately, is indicated. This is impossible since the viscosity of the asphalt used is so high that Taylor's correction for sympathetic flow, as applied by Leviton and Leighton, is insignificant. Remember-

ing the errors involved, for the plot shown the $\phi/\phi_0 - 1$ values have been again multiplied by such a factor as to make $a = 2.5$; this makes $C_{\max.} = 0.56$, approximately. No really accurate interpretation of these data can be attempted because of the scarcity of points at low concentrations, which makes it impossible definitely to establish a first order constant.

Discussion

Limiting Equations, Viscosity and Fluidity.—

It appears that for dilute suspensions meeting the requirements of Einstein's original derivation, the equation $\phi/\phi_0 = 1 - 2.5C_v$ (I) is a closer approximation than $\eta/\eta_0 = 1 + 2.5C_v$ (II). Within the limits of accuracy of available measurements, at low and even moderate concentrations, low order terms in C_v higher than the first tend to vanish when the fluidity function is used. Thus, the limiting fluidity equation describing the flow of suspensions of rigid spheres appears to be I, as given above. The limiting viscosity equation appears to be not II but the reciprocal of I, $\eta/\eta_0 = 1 + 2.5C_v + 6.25C_v^2 + \dots$ (III). This last compares with Einstein's original complete equation, $\eta/\eta_0 = 1 + 2.5C_v + 4.0C_v^2 + \dots$ (IV).

Complete Equations.—The distinction between limiting equations expanded to include hydrodynamic effects not considered by Einstein, and equations expanded merely to cover wide concentration ranges is not always clear. In some derivations the added effects have been imposed on II, not on IV. Such derivations nullify the basic hydrodynamics considered by Einstein, and are inadequate to the extent II is inadequate.

Empirical equations of the form $\phi/\phi_0 = 1 - 2.5C_v + mC_v^p - nC_v^{p+2}$ (VI), where p is at least 5, can be made to fit experimental fluidity plots over

(22) E. Rhodes and H. F. Smith, *J. Rubber Research Inst. Malaya*, **9**, 171 (1939).

(23) H. Eilers, *Kolloid. Z.*, **97**, 313 (1941).

the entire range of fluidities from 1 to zero. For Vand's extrapolated and Couette curve (Fig. 1) the equation $\phi/\phi_0 = 1 - 2.5C_v + 11C_v^5 - 11.5C_v^7$ is quite satisfactory. Apparently the first two terms suffice for flow subject to classical hydrodynamic analysis. The third and fourth terms can be interpreted as due to appearance of effects resulting from the near approach of particles. The contribution of the third term becomes significant at $C_v = 0.25$, approximately, at which concentration the least distance between spheres in cubical array is 0.218 times their diameter. The contribution of the fourth term becomes significant at $C_v = 0.45$, approximately, at which the separation distance is only 0.05 times the particle diameter. These transition concentrations may mark in turn the onset of inhibition of rotation and of interlocking.

Equations such as VI, in which the last term is negative and increases rapidly in absolute value in a certain concentration range, can be adjusted to make $\phi/\phi_0 = 0$ at and above any specific concentration, e.g., $C_v = 0.5236$; polynomials in which the last term or terms are positive give fictitious positive fluidities at high concentrations; logarithmic series give fluidities which approach zero asymptotically. In neither of the last two cases is the flow behavior indicated in accord with the facts.

Correction Factors.—The various corrections evaluated and applied directly by Vand for his glass beads, and implicitly involved in the extrapolations of his data described here, are in general numerically unimportant with true colloidal systems, e.g., gamboge, latex, sulfur sols, mushroom spores, fat suspensions, and protein solutions. If for visible particles, such as glass beads, the corrections are to a certain degree inadequate, this certainly may be due in part to the several assumptions and approximations necessary in their evaluation. It also may be due to omission of still other types of corrections. Correction of C_v for real or presumed shells of bound water, for example, would be comparable with the aggregate of the other C_v corrections used by Vand.

Applications.—The tangent to ϕ/ϕ_0 vs. C_v plots $C_v = 0$ usually can be determined graphically with considerable accuracy. The slope of this line, the reciprocal of its intercept at $\phi/\phi_0 = 0$, is the first order constant in the equation $\phi/\phi_0 = 1 - aC_v + \dots$. This constant is identical with the *intrinsic viscosity*. Its evaluation by using fluidity rather than viscosity data is the more accurate to the extent the fluidity-concentration relationship is the more linear.

Since it seems established that for rigid spherical

particles the initial slope intercept should fall at $C_v = 0.4$, as required to make $a = 2.5$, and since it appears that the actual final intercept should be in the near neighborhood of $C_v = 0.5263$, the volume fraction of spheres in cubical packing, it follows that if for a given set of data a suitable multiplier of C_v , the dry volume fraction, will give a plot with these intercepts, then the particles must be spheres and the multiplier equal to V , the voluminosity.

Voluminosity, a term proposed by Bredee,²⁴ is commonly defined as the ratio of the effective or hydrodynamic volume of a dispersed particle to the dry volume of contained colloid. As such it may include shape factors as well as corrections of the volume for hydration, solvation, and for electroviscous effects (cf. ref.²⁵). For spheres the shape factor is 2.5/2.5 or 1, making V in this case a volume correction only.

DISCUSSION

R. H. OTTEWILL (Cambridge University).—I think it is important to stress that one has to be careful about applying such viscosity-concentration relationships to systems which contain charged particles in solutions of low electrolyte concentration. For example, in some recent work of Professor Overbeek and myself on very concentrated sols of silver iodide, containing near spherical particles of radius 250 Å., the coefficients of C_v^2 and C_v^3 were found to vary considerably with rate of shear and the electrolyte concentration of the suspending medium.

T. F. FORD.—Reference to the electroviscous effect is made in the paper. It is agreed that in many systems large apparent changes in V can be brought about by changes in the ionic environment. Such changes are insignificant for the systems here discussed.

J. G. BRODNYAN (Rohm and Haas Co.).—Is there any reason why you ignored Mooney's equation which was derived using a functional method?

T. F. FORD.—Mooney's equation (*J. Coll. Sci.*, 6, 162 (1951)) is only one of many which were omitted. It could be included in Table I between Vand's and Simha's equations. The expanded forms are

$$\eta/\eta_0 = 1 + 2.5C_v + (3.125 + 2.5k)C_v^2 + \dots \text{ and } \phi/\phi_0 = 1 - 2.5C_v + (3.125 - 2.5k)C_v^2 + \dots$$

Mooney sets the value of k , for monodisperse systems, only roughly between the limits 1.35 and 1.91, the reciprocals of the volume fractions of uniform spheres in close packing and cubical packing, respectively. The actual value to be used is left for experimental determination. To fit Vand's data he makes $k = 1.43$, and to fit Eiler's data on (poly-disperse) asphalt he makes $k = 0.75$. In any case it will be seen that Mooney's equation also is more nearly linear in the fluidity form. It was omitted in the interest of brevity and because it would contribute little to the basic conclusion.

(24) H. L. Bredee and L. A. Van Bergen, *Chem. Weekblad*, 30, 223 (1933).

(25) J. T. G. Overbeek and H. G. Bungenberg de Jong, in H. G. Kruyt, "Colloid Science," Elsevier Publishing Co., Inc., New York, N. Y., 1949, Vol. II, p. 209.